

PROCESS FOR PREPARING ETHER-CAPPED POLY(OXYALKYLATED)
ALCOHOL SURFACTANTS

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Technical Field

5 The present invention relates to a process for preparing low-foaming nonionic surfactants and more particularly to a process for preparing ether-capped poly(oxyalkylated) alcohol surfactants which have superior spotting and filming benefits in dishwashing and hard surface cleaning applications, as well as suds suppression in detergent compositions.

Background of the Invention

Due to the varied nature of different cleaning compositions, different surfactants are better suited for some applications while being less suited or totally unsuitable for other applications. Nonionic surfactants, such as alcohol ethoxylates, and alkyl glucose amides are of considerable importance in detergent products. For example, under some conditions, nonionic surfactants aid cleaning of greasy soils and inhibit the formation of calcium soap. However, conventional nonionic surfactants designed for effective cleaning in laundry products form liquid crystalline phases on mixing with water. These phases can hinder the rate of mixing with water and lead to undesirable optical properties of thin films on solution drying. For example, conventional nonionics sprayed on the surface of granules to achieve target density can give rise to poor granule dissolution and residue in horizontal axis machine dispensers. Conventional nonionics formulated at high levels in liquid products can lead to poor rates of mixing with water and consumer concern. Conventional nonionics in window and floor cleaners can form visible liquid crystalline films on drying that increase the effort required by the consumer to achieve good results. Similarly, a nonionic surfactant for use in an automatic dishwashing machine would need to minimize foam production and not leave undesirable spots and films on the cleaned surfaces.

On account of the foregoing technical constraints as well as consumer needs and demands, product compositions are undergoing continual change and improvement. Moreover environmental factors such as the need for biodegradable materials, the restriction of phosphate, the desirability of providing ever-better cleaning results with less product, providing less thermal energy demand, and less water to assist the washing process, have all driven the need for improved compositions.

Accordingly, the need remains for new surfactants which are suitable for use in a variety of compositions which can provide improve dissolution of solid products (like bars and tablets) and granular products, improved rates of mixing with water as with liquid products, improved streaking and filming performance as in hard surface cleaners and automatic dishwashing, good cleaning, suds control and good biodegradability while avoiding incompatibility with other cleaning surfactants and/or bleach.

BACKGROUND ART

U.S. Patent 4,272,394, WO 94/22800, WO 93/04153, WO96/00253 and WO 98/17379.

SUMMARY OF THE INVENTION

In accordance with a first aspect of the present invention, a process for preparing an ether-capped poly(oxyalkylated) alcohol surfactant is provided. The surfactant has the formula:



wherein, R is selected from the group consisting of linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms; R¹ may be the same or different, and is independently selected from the group consisting of branched or linear C₂ to C₇ alkylene in any given molecule; x is a number from 1 to about 30; and R² is selected from the group consisting of:

- (i) a 4 to 8 membered substituted, or unsubstituted heterocyclic ring containing from 1 to 3 hetero atoms; and

(ii) linear or branched, saturated or unsaturated, substituted or unsubstituted, cyclic or acyclic, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms;

provided that when R² is (ii) then either at least one of R¹ is other than C₂ to C₃ alkylene or R² has from 6 to 30 carbon atoms.

The process comprises the steps of:

(a) providing a vinyl ether of the formula



wherein R² is as defined above;

(b) providing an alkoxyated alcohol of the formula



wherein R, R¹, and x, are as defined above;

(c) reacting said vinyl ether with said alkoxyated alcohol in the presence of a catalyst to form said ether-capped poly(oxyalkylated) alcohol.

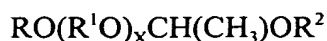
These and other aspects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (° C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Once again, the present invention is directed toward a process for producing a low-foaming nonionic surfactant for use in detergent compositions.

It has been surprisingly discovered in accordance with the present invention that significant improvements in spotting and filming characteristics and, when used in conjunction with high cloud point surfactants, in the removal of greasy soils relative to conventional surfactants, are provided via the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention.

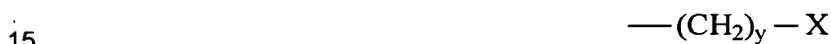
The novel surfactants of the present invention comprise ether-capped poly(oxyalkylated) alcohols having the formula:



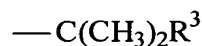
In one aspect of the present invention R is a linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon radical having from about 1 to about 20 carbon atoms, even more preferably R is a linear or branched, saturated, aliphatic hydrocarbon radicals having from about 4 to about 18 carbon atoms.

5 In one aspect of the present invention R, R¹ and R² are selected such that the ether-capped poly(oxyalkylated) alcohol surfactant contains one or more chiral carbon atoms.

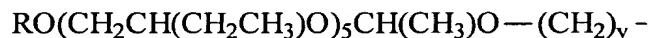
In the novel compounds of the present invention, when R² is (ii) then either at least one of R¹ is other than C₂ to C₃ alkylene or R² has from 6 to 30 carbon atoms. That is, when R² is (ii), R² is either linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 6 to about 30 carbon atoms or linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms, with at least one of R¹ is other than C₂ to C₃ alkylene. For example, when R² is a hydrocarbon of the formula:



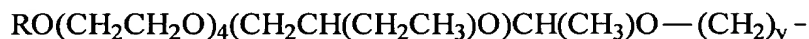
where, y and X are described hereafter, or R² is a hydrocarbon radical of the formula:



where, R³ is described hereafter, then at least one of R¹ is other than C₂ to C₃ alkylene. For example, if x is 5, and R² was (CH₂)_y-X, then the ether-capped poly(oxyalkylated) alcohol could have the formula:

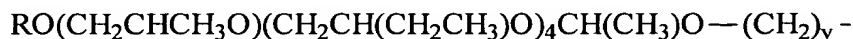


or



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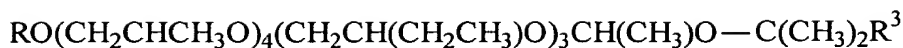
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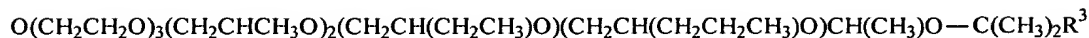
Similarly, for example if R² was -C(CH₃)₂R³ and x was 7, then the ether-capped poly(oxyalkylated) alcohol could have the formula:



or



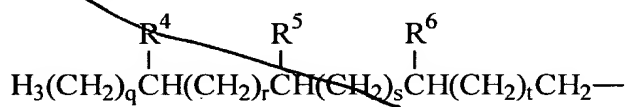
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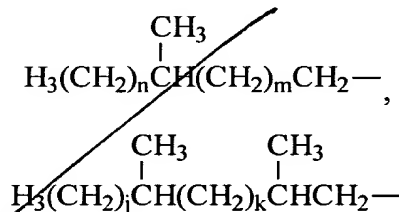
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These examples are included merely for illustrative purposes and are not to be construed in any manner as limiting of the scope of the present invention.

In one aspect of the present invention, R is a hydrocarbon radical of the formula:

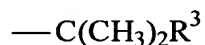


wherein R^4 , R^5 , and R^6 are each independently selected from hydrogen, and C_1 - C_3 alkyl, , more preferably hydrogen, C_1 - C_2 alkyl, even more preferably hydrogen, and methyl, provided that R^4 , R^5 , and R^6 are not all hydrogen and, when t is 0, at least R^4 or R^5 is not hydrogen; q , r , s , t are each independently integers from 0 to 13. In one more preferred form of this aspect R is selected from the formulas:



wherein n , m , j and k are each independently integers from 0 to 13.

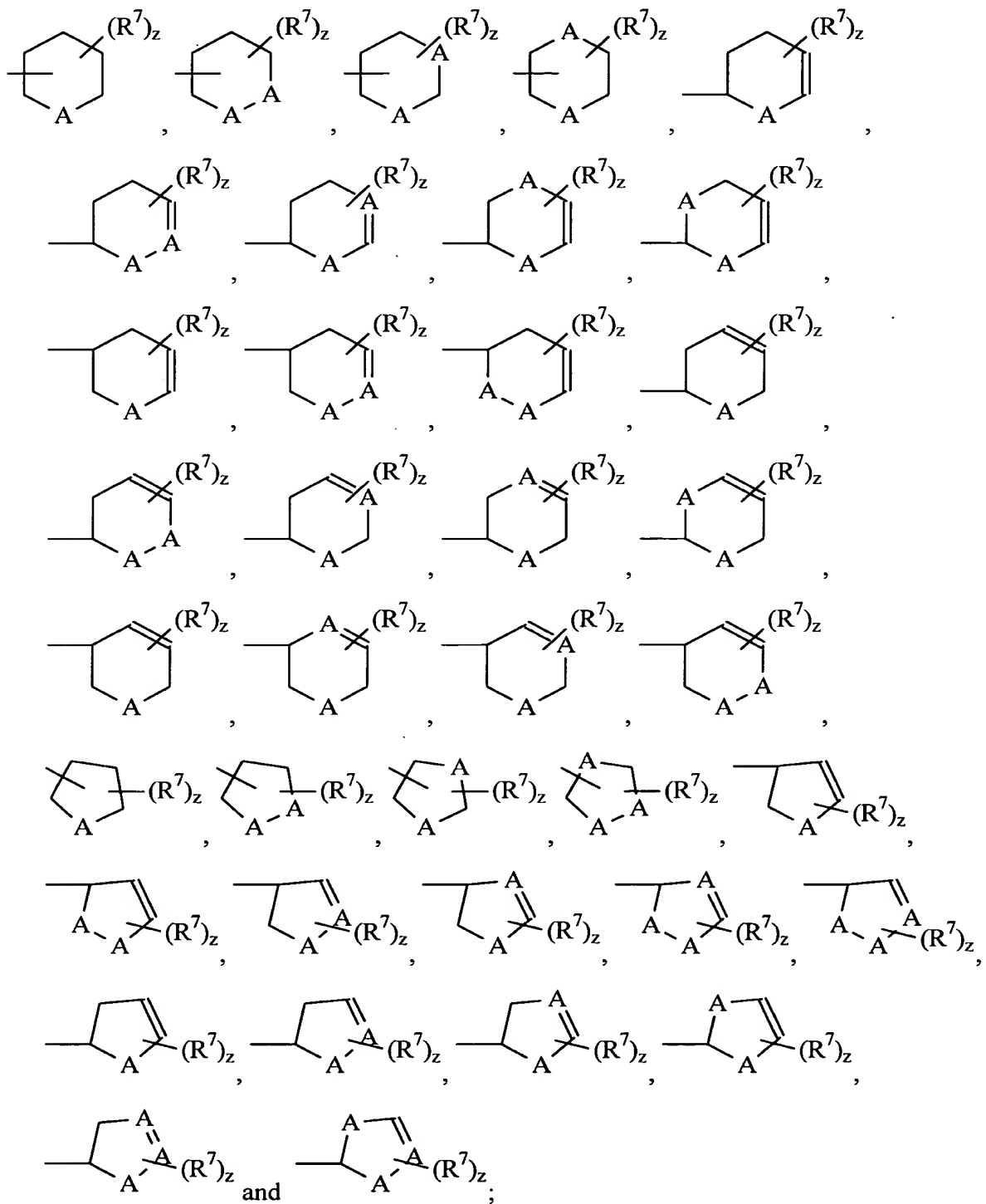
In one aspect of the present invention R^2 is a hydrocarbon radical of the formula:



R^3 is selected from the group consisting of linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30, more preferably 1 to 20, even more preferably 1 to 15, carbon atoms,. In one embodiment of this aspect of the present invention, R^3 is ethyl.

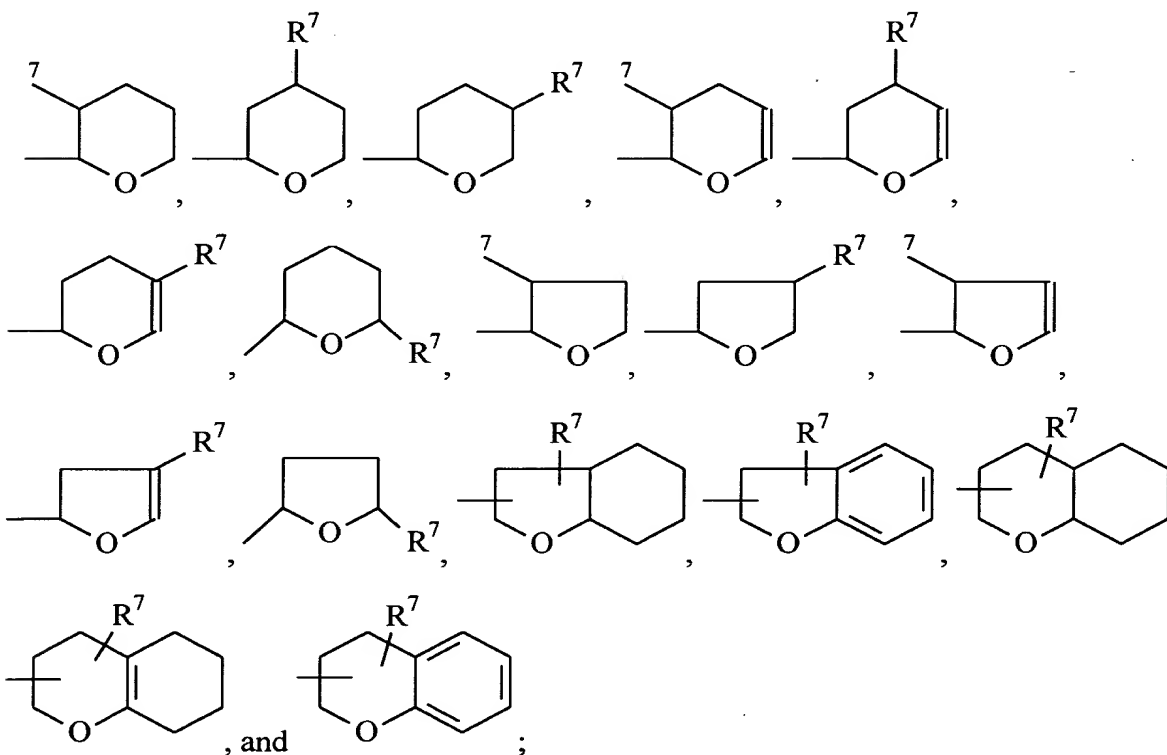
In one aspect of the present invention R^2 is a 4 to 8 membered substituted, or unsubstituted heterocyclic ring containing from 1 to 3 hetero atoms. In one embodiment of this aspect of the invention the hetero atoms are selected from the group comprising

oxygen, nitrogen, sulfur and mixtures thereof. In one embodiment of this aspect of the invention R^2 is a 5 or 6 member heterocycle. In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:



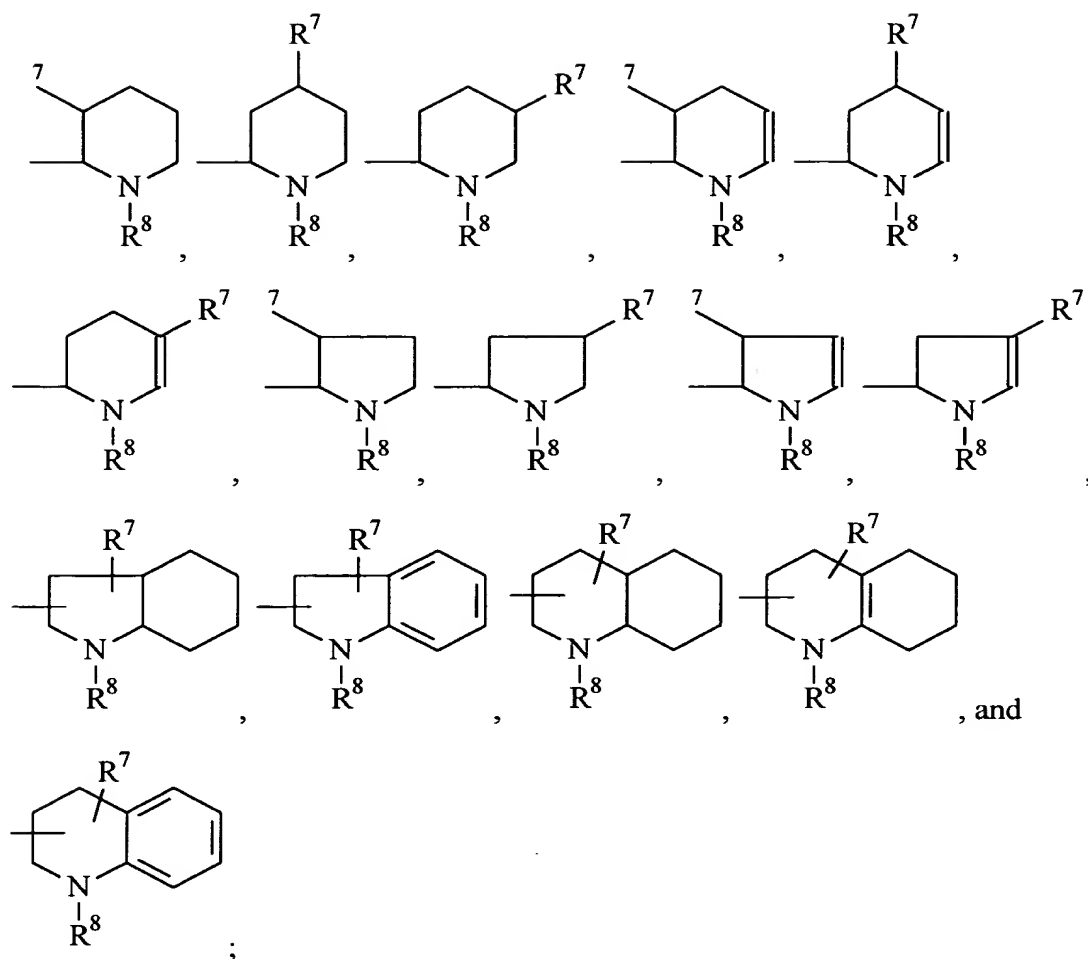
- wherein each R^7 is independently selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon or alkoxy radical having from about 1 to about 10 carbon atoms, or R^7 is a saturated or unsaturated, substituted or unsubstituted, alicyclic or aromatic hydrocarbon radical having, from about 1 to about 10 carbon atoms, which is fused to the heterocyclic ring; each A is independently selected from the group consisting of O, and $N(R^8)_a$, wherein R^8 is independently selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon radical having from about 1 to about 10 carbon atoms, and a is either 0 or 1; z is an integer from 1 to 3.

In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:



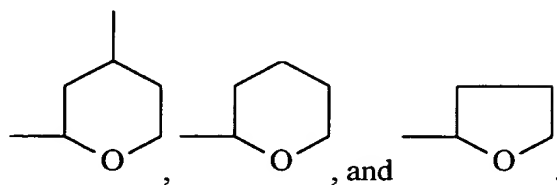
wherein R^7 is defined as above.

In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:

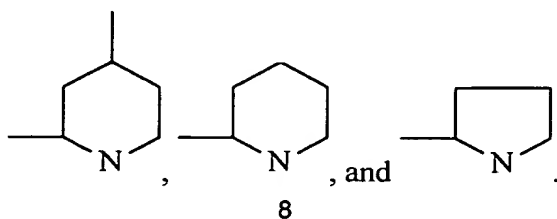


5 wherein R^7 and R^8 are defined as above.

In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:

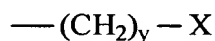


10 In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:



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In one aspect of the present invention R² is a hydrocarbon of the formula:



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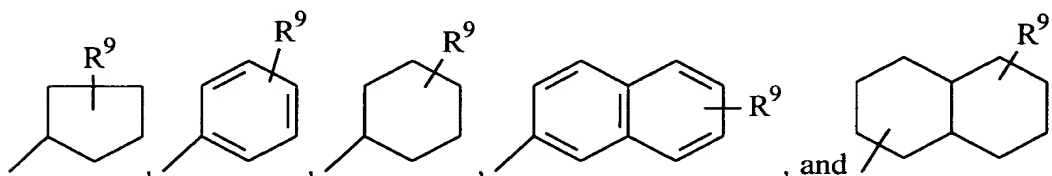
In another embodiment of this aspect of the present invention X is selected from the group consisting of:



wherein each R⁹ is independently selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon

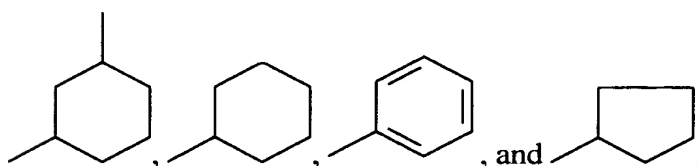
or alkoxy radical having from about 1 to about 10 carbon atoms, or R^9 is a saturated or unsaturated, substituted or unsubstituted, alicyclic or aromatic hydrocarbon radical having, from about 1 to about 10 carbon atoms, which is fused to the ring; w is an integer from 1 to 3.

- 5 In another embodiment of this aspect of the present invention X is selected from the group consisting of:



wherein R^9 is defined as above.

- 10 In another embodiment of this aspect of the present invention X is selected from the group consisting of:



- 15 In one aspect of the present invention R^2 is a linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms, more preferably R^2 is a linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon radical having from about 1 to about 20 carbon atoms, even more preferably R^2 is a linear or branched, saturated, aliphatic hydrocarbon radicals having from about 4 to about 18 carbon atoms.

- 20 In one aspect of the present invention, when x is greater than 2, R^1 may be the same or different. That is, R^1 may vary between any of the alkyleneoxy units as described above. For instance, if x is 3, R^1 may be selected to form ethyleneoxy(EO) or propyleneoxy(PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and the variation may be much larger with a higher
25 integer value for x and include, for example, multiple (EO) units and a much small

number of (PO) units. Similarly, ethylene, and propylene are chosen for example only and the variation may be much larger with selection of linear or branched butylene, pentylene, hexylene and/or heptylene.

The surfactants of the present invention can be prepared via a variety of different processes. In one aspect of the present invention, the surfactants may be prepared by reacting a vinyl ether of the formula:



wherein R^2 is as defined above; with an alkoxyated alcohol of the formula



wherein R , R^1 , and x , are as defined above, in the presence of a catalyst to form the ether-capped poly(oxyalkylated) alcohol.

In one embodiment of this aspect of the present invention the step of reacting of vinyl ether with alkoxyated alcohol is conducted in the presence of a catalyst. Suitable catalysts include Lewis acids; acids and their salts, both organic and inorganic; pyridinium salts; polymers; clays, such as, Spanish sepiolite clay, GIRDLER K-10; aluminosilicates or zeolites, such as HZS-360 zeolite, H-Y zeolite; activated carbon, such as sulfonated charcoal; transition metal complexes, such as, molybdenyl(VI) acetylacetonate; transition metal salts, such as lanthanum trichloride, ceric ammonium nitrate; 2,3-dichloro-5,6-dicyano-p-benzoquinone; bis(trimethylsilyl)sulfate, and mixtures thereof.

Suitable Lewis acids include, but are not limited to, $TiCl_4$, $Ti(O^iPr)_4$, $ZnCl_2$, $SnCl_2$, $AlCl_3$, platinum dichloride, copper(II) chloride, phosphorous pentachloride, phosphorous trichloride, cobalt(II) chloride, zinc oxide, iron(II) chloride and $BF_3 \cdot OEt_2$.

Suitable inorganic acids include, mineral acids, such as, phosphoric acid, sulfuric acid, hydrochloric acid, phosphorous oxychloride, aluminium phosphate and ammonium chloride. Furthermore, the mineral acids or their salts can optionally be adsorbed on to a substrate, such as, silica gel, or alumina. For example sulfuric acid adsorbed on silica gel, or alumina impregnated with zinc chloride.

Suitable organic acids include: carboxylic acids, such as, acetic acid, oxalic acid, glycolic acid, citric acid, tartaric acid, maleic acid and oxydisuccinic acid; halogenated

carboxylic acids, such as, trifluoroacetic acid, heptafluorobutyric acid, dichloroacetic acid, and trichloroacetic acid; and sulfonic and sulfinic acids and their salts such as, p-toluenesulfonic acid, p-toluenesulfinic acid, methanesulfonic acid, trifluoromethanesulfonic acid, 4-bromobenzene sulfonic acid, naphthalene sulfonic acid, 5 (+)-10-camphor sulfonates, and alkyl benzene sulfonic acid.

Suitable pyridinium salts, include, but are not limited to, pyridinium p-toluenesulfonate (PPTS), pyridinium p-toluenesulfinate, pyridinium hydrochloride, pyridinium hydrobromide, pyridinium hydrogen bisulfate, pyridinium hydrogen sulfate and mixtures thereof.

10 Suitable transition metal, include, but are not limited to, molybdenyl(VI) acetylacetonate; transition metal salts, such as lanthum trichloride, ceric ammonium nitrate; 2,3-dichloro-5,6-dicyano-p-benzoquinone, mercury(II) acetate, mercury(II) trifluoroacetate, copper(II) acetylacetonate and tetracarbonylbis(cyclopentadienyl)diiron.

15 Suitable polymers, include, but are not limited to, polymeric ion exchange resins, or polyvinyl pyridines. Suitable polymeric ion exchange resins include those of the Amberylst series, such as AMBERYLST®15, available from Rohm & Haas, the DOWEX® series, such as, DOWEX 50X8-50 available from Dow; REILLEX 424, available from Reilly Industries; the Amberlite series, such as AMBERLITE IRA-400, or AMBERLITE IR-118, available from Rohm & Haas; available from United Catalyst ; the 20 ENVIROCAT series, such as ENVIROCAT EPZG, available from Contract Chemicals; and combinations thereof. Suitable polyvinyl pyridines can be unsubstituted or substituted, such as substituted on the vinyl group and/or on the pyridine ring. Examples of suitable polyvinyl pyridines include, but are not limited to, poly(4-vinylpyridine trifluoromethanesulfonate), poly(2-vinylpyridine trifluoromethanesulfonate), poly(4- 25 vinylpyridine p-toluenesulfonate), poly(2-vinylpyridine p-toluenesulfonate), poly(4-vinylpyridine chloride), poly(2-vinylpyridine chloride), poly(4-vinylpyridine bromide), poly(2-vinylpyridine bromide), and mixtures thereof. These polymeric catalysts have the additional advantage of being easy to separate from the surfactant produced.

30 Other suitable catalysts include, bis(trimethylsilyl)sulfate, iodotrimethylsilane, allyltrimethyl silane, hexamethyldisilane, iodine, bromine, iron(II) sulfate,

triphenylphosphine, aluminium sulfate, alkylether sulfuric acids, alkyl sulfuric acids, lithium perchlorate, lithium tetrafluoroborate, acetonitriletriphenylphosphonium bromide, zirconium hydroxide, potassium cyanide, and platinum oxide.

Preferred catalysts include the sulfonic acids, Lewis acids, polyvinyl pyridines, methanesulfonic acid, AMBERYLST®15, acidic versions of DOWEX® and pyridinium p-toluenesulfonate (PPTS) with polyvinyl pyridines, pyridinium p-toluenesulfonate (PPTS), p-toluenesulfonic acid, DOWEX®, AMBERYLST®15 and methanesulfonic acid, being the most preferred.

Mixtures of catalysts are also within the scope of the present invention. Similarly, the uses of supported, such as in a column for a continuous reaction, and unsupported catalysts are also within the scope of the present invention.

The catalysts are preferably employed at amounts of about 0.1 mol % to about 20.0 mol %, more preferably from about 0.1 mol % to about 10.0 mol %, even more preferably from about 0.1 mol % to about 5.0 mol %, even more preferably still from about 0.1 mol % to about 2.0 mol %, even more preferably still from about 0.2 mol % to about 1.0 mol %. Other suitable catalysts can be found in US patent No. U.S. Patent 4,272,394, and in PCT publications, WO 94/22800, WO 93/04153, WO96/00253 and WO 98/17379 all of which are incorporated herein by reference.

In one embodiment of this aspect of the present invention the reaction is conducted in the presence of a solvent, or mixtures of solvents. It is preferred that the solvent be a polar aprotic solvent. Suitable solvents include, but are not limited to, hexane, benzene, toluene, xylene, mesitylene, dichloromethane, tetrahydrofuran, dioxane, chloroform, diethylether, methyl tert-butylether, acetone, acrylonitrile, or the like. Furthermore, the reaction is preferably conducted at temperatures ranging from about -20°C to about 300°C, and more preferably from about -10°C to about 250°C. Lastly, the reaction is preferably conducted at pressures ranging from about 0.5 atmospheres to about 100 atmospheres, and more preferably from about 0.8 atmospheres to about 10 atmospheres.

In another embodiment of this aspect of the present invention the step of reacting vinyl ether with alkoxylated alcohol is conducted in the absence of a solvent.

Further disclosure on suitable solvents and catalysts can be found in "Advanced Organic Chemistry", by Jerry March, 4th ed., Wiley-Interscience, 1992, "Comprehensive Organic Transformations" by Richard C. Larock, VCH Publishers, 1989, and "Protective Groups in Organic Synthesis" 3RD ed. by Theodora W. Greene and Peter G. M. Wuts, Wiley-Interscience, 1999 the relevant portions of which are incorporated herein by reference.

In one embodiment of the present invention, the process is performed as a batch process. That is, the reaction is let proceeded to completion, or near completion, and then final product is removed. In another embodiment of the present invention, the process is performed as a continuous process. That is, the product of the process is continuously removed from the reaction vessel while staring material is added at a comparable rate.

In one embodiment of the present invention the vinyl ether is reacted with the alkoxyated alcohol at a mole ratio of from about 5 to about 1, more preferably from about 3 to about 1, more preferably still from about 1.5:1 to about 0.90:1 mole %.

In one embodiment of the process of the present invention the process may be conducted in an inert gas. This may be done by sparging with any suitable inert gas, such as nitrogen, helium, neon, or argon.

In one embodiment of the present invention reaction step (c) may be followed by optional step (d). Step (d), is a step in which the reaction step (c) is quenched, preferably by the addition of base. The amount of the ether capped poly(oxyalkylated) alcohol surfactant present in the reaction mixture will depend upon many factors, including but not limited to, starting materials, temperature, catalyst selection and the like. Quenching stops the reaction, of the starting materials, and ensures that any ether capped poly(oxyalkylated) alcohol surfactant produced does not undergo further reaction or revert back to the starting materials. The quenching of step (c) produces a mixture which contains ether capped poly(oxyalkylated) alcohol surfactant, as well as, unreacted starting materials, catalyst and the products of any side reactions. In one embodiment of this present invention the quenching of the reaction of step (c) is done when the reaction mixture preferably contains at least 90%, more preferably 95% by weight of ether capped poly(oxyalkylated) alcohol surfactant. The remaining 10%, more preferably 5% by

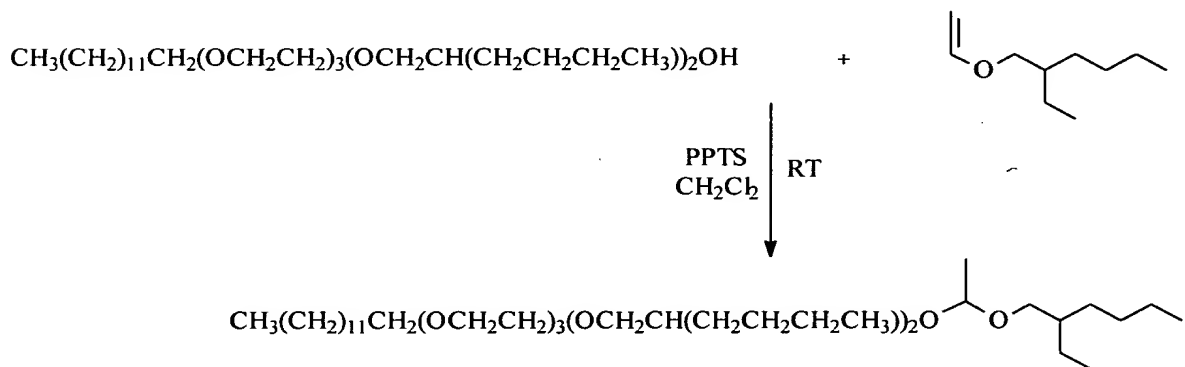
weight, comprises, unreacted starting material as well as products of side reactions, such as byproduct acetals. In one aspect of this embodiment of the present invention the base may be optionally selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates alkali metal hydroxides, alkali metal alcoholates, alkanolamines, 5 alkylamines, aromatic amines and mixtures thereof. In a further aspect of the present invention the base may be optionally selected from the group consisting of potassium carbonate, sodium carbonate, sodium bicarbonate sodium methoxylate, sodium ethoxylate, potassium tert-butyloxylate, triethylamine, triethanolamine and mixtures thereof. In another aspect of this embodiment of the present invention the base may be in 10 the form of an aqueous solution. In a further aspect of this embodiment of the present invention the aqueous solution may be at a temperature of from about 20°C to about 60°C.

The expression "product of step (c)" is meant to include not only the ether-capped poly(oxyalkylated) alcohol surfactant but also any unreacted starting materials or any 15 materials produced from side reactions, such as dimers, which would be present at the conclusion of step (c).

In one embodiment of the present invention the process of the present invention may optionally further comprise a step (e). Step (e) is removal of color bodies and/or odors from the product of steps (c), or (d). In one aspect of this embodiment of the 20 present invention removal of the color bodies and/or odors is obtained by contacting the product of steps (c) or (d) with a reagent. The reagent can either be an oxidant, or a reductant. Suitable oxidants include hydrogen peroxide. Suitable reductants include sodium borohydride, and hydrogen over a palladium/carbon catalyst. In a further aspect of this embodiment of the present invention the color bodies and/or odors are removed by 25 contacting the product of steps (c) or (d) first with an oxidant and then a reductant or first with a reductant and then an oxidant.

In one embodiment of the present invention the ether-capped poly(oxyalkylated) alcohol surfactant produced in step (c) may optionally removed from the product of step (c) by centrifuging.

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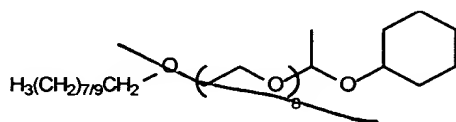


removing water and the last traces of 1,2-epoxybutane under vacuum and cooling to ambient, methylene chloride (200 ml) and 2-ethylhexyl vinyl ether (19.49 g, 124.7 mmol) are added. The mixture is cooled to 0°C and pyridinium *p*-toluenesulfonate (0.42 g, 1.7 mmol) is added. The mixture is first stirred 4 h at 0°C and then 18 h at ambient. After diluting with diethyl ether (200 ml), the mixture is washed twice with saturated sodium bicarbonate and the organic layer dried with sodium sulfate/potassium carbonate. The product was concentrated by rotary evaporation and dried under vacuum in the presence of potassium carbonate to yield a yellow liquid.

Example 2

Examples 2(a) to (i) are illustrative of some of the possible catalysts, work up options and relative amounts the starting materials that can be used in the present invention.

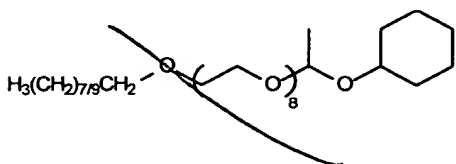
Example 2(a)



Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

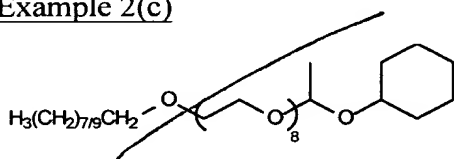
Neodol 91-8 (20.00 g, 39.1 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, methylene chloride (100 ml) and cyclohexyl vinyl ether (5.43 g, 43.01 mmol) are added. The mixture is cooled to 0°C and pyridinium *p*-toluenesulfonate (0.43 g, 1.6 mmol) is introduced into the flask. The mixture is first stirred 4 h at 0°C and then 18 h at ambient. The product mixture is then washed twice with saturated sodium bicarbonate and the organic layer dried over sodium carbonate, concentrated by rotary evaporation and further stripped under vacuum at 60°C (0.1 mmHg) in the presence of potassium carbonate to yield a liquid.

Example 2(b)

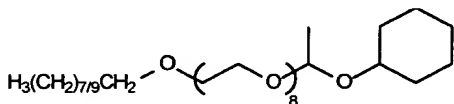


Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

- Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (0.43 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, cyclohexyl vinyl ether (4.94 g, 39.1 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is filtered to yield a liquid.

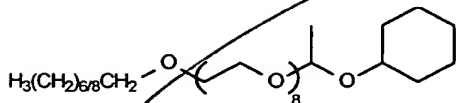
Example 2(c)

- Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal
- Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (0.43 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, cyclohexyl vinyl ether (4.94 g, 39.1 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is separated from the catalyst by centrifugation to yield a liquid.

Example 2(d)Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

- Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (0.43 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, cyclohexyl vinyl ether (4.94 g, 39.1 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is washed with 20% potassium carbonate solution, dried and filtered to yield a liquid.

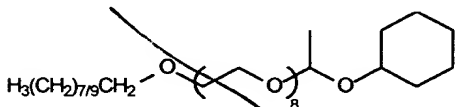
Example 2(e)



Preparation of $C_{8/10}H_{17/21}EO_8$ -cyclohexyl acetal

Alcohol ethoxylate $C_{8/10}H_{17/21}EO_8$ (20.00 g, 40.2 mmol) and poly(4-vinylpyridinium chloride) (2.0 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, cyclohexyl vinyl ether (5.07 g, 40.2 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is filtered to yield a liquid.

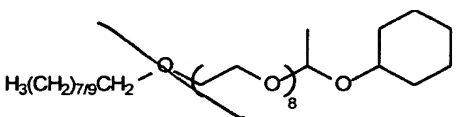
Example 2(f)



Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (7.82 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, acetone (150 mL) and cyclohexyl vinyl ether (4.94 g, 39.1 mmol) are added. The mixture is stirred for three days, filtered and concentrated by rotary evaporation to yield a liquid.

Example 2(g)

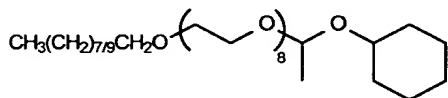


Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

Neodol 91-8 (20.00 g, 39.1 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, methylene chloride (100 ml) and cyclohexyl vinyl ether (4.84 g, 38.4 mmol) are added. The mixture is cooled to 0°C and pyridinium p-toluenesulfonate (0.39 g, 1.5 mmol) is introduced into the flask. The mixture is first stirred 4 h at 0°C and then 18 h at

ambient. The product mixture is then washed twice with saturated sodium bicarbonate and the organic layer dried over sodium carbonate, concentrated by rotary evaporation and further stripped under vacuum at 60°C (0.1 mmHg) in the presence of potassium carbonate to yield a liquid.

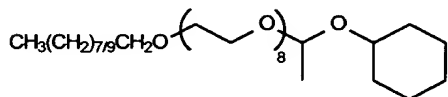
5 Example 2(h)



Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

Neodol 91-8 (20.00 g, 39.1 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient, cyclohexyl vinyl ether (5.04 g, 39.9 mmol) is added. *p*-Toluenesulfonic acid monohydrate (0.112 g, 0.59 mmol) is added to the mixture and stirred to dissolve. An exotherm is observed starting from 22°C and ending at 30°C, with the development of a precipitate. After 16 minutes of reaction time, the reaction pH is adjusted to ≥7 with triethanolamine, filtered and then stripped in a Kugelrohr oven (50°C, 0.1 mm Hg) to yield a quantitative amount of a near colorless liquid.

Example 2(i)

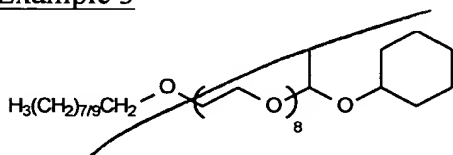


Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

Neodol 91-8 (900.0 g, 1.76 mol) is placed into a 3 L three-necked rounded bottomed flask, fitted with a heating mantle, mechanical stirrer, internal thermometer, and vacuum/argon take-off adapter. The contents are dried under vacuum at 80 °C for 30 min. A portion of the dry Neodol 91-8 (20 g) is set aside after the contents are cooled to room temperature. Cyclohexylvinyl ether (217.82 g, 1.73 mol) is then added to the reaction mixture. The reagents are cooled to about 10 °C at which point methanesulfonic acid (1.80 mL) and the 20 g portion of Neodol set aside are combined and added to the reaction mixture via syringe, subsurface, in one portion. The reaction mixture exotherms, ice bath controlled, to 22 °C. After 1h, the mixture is quenched with 15% sodium

carbonate solution (35 mL). The mixture is placed under vacuum by stripping in a Kugelrohr oven (25 °C, 0.1 mm Hg) for 10 min. The product is filtered to yield a quantitative amount of a near colorless liquid.

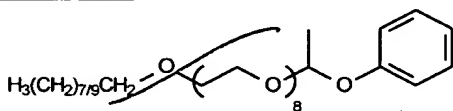
5 Example 3



Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

The procedure of Example 2(i) is repeated with the substitution of Neodol 91-8 for Neodol 1-7.

10 Example 4

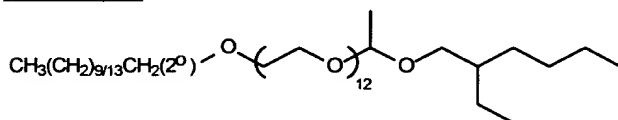


Preparation of $C_{9/11}H_{19/23}EO_8$ -benzyl acetal

The procedure of Example 3 is repeated with the substitution of benzyl vinyl ether for cyclohexyl vinyl ether.

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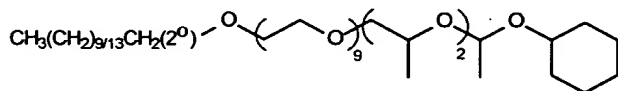
Example 5



Preparation of $C_{11/15}H_{23/31}EO_{12}$ -2-ethylhexyl acetal

The procedure of Example 2(i) is repeated with the substitution of 2-ethylhexyl vinyl ether for cyclohexyl vinyl ether and Tergitol-15-S-12 for Neodol 1-7.

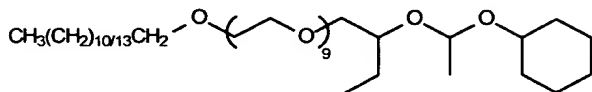
Example 6



Preparation $C_{11/15}H_{23/31}EO_9PO_2$ -cyclohexyl acetal

The procedure of Example 1 is repeated with the substitution of propylene oxide for 1,2-epoxybutane, cyclohexyl vinyl ether for 2-ethylhexyl vinyl ether, and Tergitol 15-S-9 for Neodol 1-7.

5 Example 7

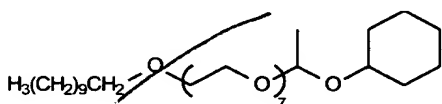


Preparation of $\text{C}_{12/15}\text{H}_{25/31}\text{EO}_9\text{BO}_1$ -cyclohexyl acetal

The procedure of Example 1 is repeated with the substitution of cyclohexyl vinyl ether for 2-ethylhexyl vinyl ether and Neodol 25-9 for Neodol 1-7.

10

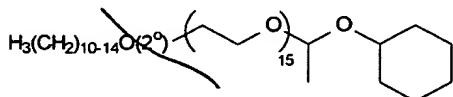
Example 8



Preparation of $\text{C}_{11}\text{H}_{23}\text{EO}_7$ -cyclohexyl acetal

Neodol 1-7 (50.00 g, 104.0 mmol) is placed into a 1000 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, methylene chloride (500 ml) and cyclohexyl vinyl ether (6.55g, 51.9 mmol) are added. The mixture is cooled to 0°C and pyridinium *p*-toluenesulfonate (1.04 g, 4.2 mmol) is introduced into the flask. The mixture is first stirred 4 h at 0°C and then 18 h at ambient. The product mixture is then washed twice with saturated sodium bicarbonate and the organic layer dried with magnesium sulfate, concentrated by rotary evaporation and further stripped under vacuum at 60°C (0.1 mmHg) to yield a liquid.

Example 9



25 Preparation of $\text{C}_{11/15}\text{H}_{23/31}\text{EO}_{15}$ -cyclohexyl acetal

Tergitol 15-S-15 (100.0 g, 193.8 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer, and

vacuum/argon take-off adapter. The contents are dried under vacuum at 80 °C for 10 min. A portion of the dry Tergitol 15-S-15 (2 g) is set aside after the contents are cooled to room temperature. Cyclohexyl vinyl ether (24.21 g, 191.9 mmol) is then added to the reaction mixture. The reagents are cooled to about 15 °C at which point methanesulfonic acid (0.28 g, 2.9 mmol) and the 2 g portion of Tergitol 15-S-15 set aside are combined and added to the reaction mixture via syringe, subsurface and in one portion. The reaction mixture exotherms to 40 °C. After 5 minutes, the reaction pH is adjusted to ≥ 7 with 15% sodium carbonate. The mixture is placed under vacuum by stripping in a Kugelrohr oven (50 °C, 0.1 mm Hg) for 10 min. The product is filtered to yield a quantitative amount of a near colorless liquid.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. The ether-capped poly(oxyalkylated) alcohol surfactant produced by the process of the present invention may be used in other applications, such as a wetting agents, antifoaming agents, drilling muds, etc., in a wide range of fields, such as in biocides, pharmaceuticals, etc. Further examples of possible application for these surfactants can be found in "Nonionic Surfactants" edited by Martin J. Schinck, Surfactant Science Series, Mancel Dekker, NY, Volume 1; "Nonionic Surfactants: Physical Chemistry" edited by Martin J. Schinck, Surfactant Science Series, Mancel Dekker, NY, Volume 23; "Nonionic Surfactants: Polyoxyalkylen Block Copolymers" edited by Vaughn M. Nace, Surfactant Science Series, Mancel Dekker, NY, Volume 60; and L.G. Lundsted and I.R. Schmolka, in "Block and Graft Copolymerization", Vol. 2 (R.J. Ceresa, ed.), John Wiley & Sons, Ltd., London, 1976, pp.113-272. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

FORMULATION EXAMPLES

In the following Examples, the abbreviations for the various ingredients used for the compositions have the following meanings.

LAS Sodium linear C₁₂ alkyl benzene sulfonate

	MBAS _x	Mid-chain branched primary alkyl (average total carbons = x) sulfate
	MBAE _x S _z	Mid-chain branched primary alkyl (average total carbons = z) ethoxylate (average EO = x) sulfate, sodium salt
5	MBAE _x	Mid-chain branched primary alkyl (average total carbons = x) ethoxylate (average EO = 8)
	TFAA	C16-18 alkyl N-methyl glucamide
	CxyEzS	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
10	CxyFA	C _{1x} -C _{1y} fatty acid
	CxyEz	A C _{1x-1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
	C24 N-Me Glucamide	C ₁₂ -C ₁₄ N-methyl glucamide
	CxAPA	Alkyl amido propyl amine
15	Citric acid	Anhydrous citric acid
	Carbonate	Anhydrous sodium carbonate with a particle size between 200µm and 900µm
	Citrate	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850 µm
20	Protease	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
	Cellulase	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
	Amylase	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
25	Lipase	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
	Endolase	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S

	PB1	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
	NOBS	Nonanoyloxybenzene sulfonate in the form of the sodium salt.
	DTPMP	Diethylene triamine penta (methylene phosphonate),
5		marketed by Monsanto under the Trade name Dequest 2060
	MEA	Monoethanolamine
	PG	Propanediol
	EtOH	Ethanol
	Brightener 1	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
10	Brightener 2	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
	Silicone antifoam	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
15	NaOH	Solution of sodium hydroxide
	DTPA	Diethylene triamine pentaacetic acid
	NaTS	Sodium toluene sulfonic acid
	Fatty Acid (C12/14)	C12-C14 fatty acid
	Fatty Acid (TPK)	Topped palm kernel fatty acid
20	Fatty Acid (RPS)	Rapeseed fatty acid
	Borax	Na tetraborate decahydrate
	PAA	Polyacrylic Acid (mw = 4500)
	PEG	Polyethylene glycol (mw=4600)
	MES	Alkyl methyl ester sulfonate
25	SAS	Secondary alkyl sulfate
	NaPS	Sodium paraffin sulfonate
	C45AS	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
	CxyAS	Sodium C _{1x} -C _{1y} alkyl sulfate (or other salt if specified)

	AQA	$R_2.N^+(CH_3)_x((C_2H_4O)yH)z$ with $R_2 = C_8 - C_{18}$ where $x + z = 3$, $x = 0$ to 3 , $z = 0$ to 3 , $y = 1$ to 15 .
	STPP	Anhydrous sodium tripolyphosphate
5	Zeolite A	Hydrated Sodium Aluminosilicate of formula $Na_{12}(Al_0Si_2O_7)_n \cdot 27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
	NaSKS-6	Crystalline layered silicate of formula $\delta - Na_2Si_2O_5$
	Bicarbonate	Anhydrous sodium bicarbonate with a particle size distribution between 400 μ m and 1200 μ m
10	Silicate	Amorphous Sodium Silicate ($SiO_2:Na_2O$; 2.0 ratio)
	Sulfate	Anhydrous sodium sulfate
	PAE	ethoxylated tetraethylene pentamine
	PIE	ethoxylated polyethylene imine
	PAEC	methyl quaternized ethoxylated dihexylene triamine
15	MA/AA	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
	CMC	Sodium carboxymethyl cellulose
	Protease	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
20	Cellulase	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
	Amylase	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
25	Lipase	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
	Percarbonate	Sodium Percarbonate of nominal formula $2Na_2CO_3 \cdot 3H_2O_2$
	NaDCC	Sodium dichloroisocyanurate
	TAED	Tetraacetythylenediamine

	DTPMP	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under Tradename Dequest 2060
	Photoactivated bleach	Sulfonated Zinc Phthalocyanine bleach encapsulated in dextrin soluble polymer
5	HEDP	1,1-hydroxyethane diphosphonic acid
	SRP 1	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
	SRP 2	sulfonated ethoxylated terephthalate polymer
	SRP 3	methyl capped ethoxylated terephthalate polymer
10	Isofol 16	Condea trademark for C16 (average) Guerbet alcohols
	CaCl ₂	Calcium chloride
	MgCl ₂	Magnesium chloride
	DTPA	Diethylene triamine pentaacetic acid

15 EXAMPLES 10A to 10E: Nonaqueous Liquid Laundry Detergent compositions

Non-limiting examples of bleach-containing nonaqueous liquid laundry detergent are prepared as follows.

Preparation of LAS Powder for Use as a Structurant

Sodium C₁₂ linear alkyl benzene sulfonate (NaLAS) is processed into a powder
 20 containing two phases. One of these phases is soluble in the non-aqueous liquid detergent compositions herein and the other phase is insoluble. It is the insoluble fraction which serves to add structure and particle suspending capability to the non-aqueous phase of the compositions herein.

NaLAS powder is produced by taking a slurry of NaLAS in water (approximately
 25 40-50% active) combined with dissolved sodium sulfate (3-15%) and hydrotrope, sodium sulfosuccinate (1-3%). The hydrotrope and sulfate are used to improve the characteristics of the dry powder. A drum dryer is used to dry the slurry into a flake. When the NaLAS is dried with the sodium sulfate, two distinct phases are created within the flake. The insoluble phase creates a network structure of aggregate small particles (0.4-2 um) which
 30 allows the finished non-aqueous detergent product to stably suspend solids.

The NaLAS powder prepared according to this example has the following makeup shown in Table I.

TABLE I
LAS Powder

<u>Component</u>	<u>Wt. %</u>
NaLAS	85%
Sulfate	11%
Sulfosuccinate	2%
Water	2.5%
Unreacted, etc.	balance to 100%
% insoluble LAS	17%
# of phase (via X-ray diffraction)	2

5

Non-aqueous based heavy duty liquid laundry detergent compositions which comprise the capped nonionic surfactants of the present invention are presented below.

Component	A	B	C	D	E
LAS, From Example I	15	15	15	15	5
Nonionic from example 1	21.5	15	-	5	-
Nonionic from example 3	-	-	-	-	25
Nonionic from example 4	-	-	10	5	-
C12,13EO5	-	6.5	11.5	16.5	6.5
BPP	19.5	19	19	19	19
Sodium citrate dihydrate	7	7	7	7	7
Bleach activator	6	6	6	6	6

Sodium carbonate	9	9	9	9	9
Maleic-acrylic copolymer	3	3	3	3	3
Colored speckles	0.4	0.4	0.4	0.4	0.4
EDDS	1	1	1	1	1
Cellulase Prills	0.1	0.1	0.1	0.1	0.1
Amylase Prills	0.4	0.4	0.4	0.4	0.4
Ethoxylated diamine quat	1.3	1.3	1.3	1.3	1.3
Sodium Perborate	12	12	12	12	12
Optionals including: brightener, colorant, perfume, thickener, suds suppressor, colored speckles etc.	balance	balance	balance	balance	balance
	100%	100%	100%	100%	100%

The resulting compositions are stable, anhydrous heavy-duty liquid laundry detergents which provide excellent rates of mixing with water as well as good stain and soil removal performance when used in normal fabric laundering operations.

5

EXAMPLE 11: Hand Dishwashing Liquid compositions

The following examples further illustrate the invention herein with respect to a hand dishwashing liquid.

	<u>Ingredient</u>	<u>% (wt.)</u>	<u>Range (% wt.)</u>
10	Nonionic from example 8	5.0	1 - 20
	MBAE ₂ S ₁₅	2.0	0.5-10
	Ammonium C ₁₂₋₁₃ alkyl sulfate	7.0	2-35
	C ₁₂ -C ₁₄ ethoxy (1) sulfate	20.5	5-35
	Coconut amine oxide	2.6	2-5
15	Betaine/Tetronic 704®**	0.87-0.10	0-2 (mix)
	Alcohol Ethoxylate C ₉₋₁₁ E ₉	1.0	0.5-10

	Ammonium xylene sulfonate	4.0	1-6
	Ethanol	4.0	0-7
	Ammonium citrate	0.06	0-1.0
	Magnesium chloride	3.3	0-4.0
5	Calcium chloride	2.5	0-4.0
	Ammonium sulfate	0.08	0-4.0
	Perfume	0.18	0-0.5
	Maxatase® protease	0.50	0-1.0
	Water and minors	-----Balance-----	

10 ** Cocoalkyl betaine.

EXAMPLES 12 to 16: Shampoo compositions

		<u>Example Number</u>				
	<u>Component</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>
	Ammonium laureth-2 sulfate	5	3	2	10	8
15	Ammonium lauryl sulfate	5	5	4	5	8
	Nonionic from example 3	2	0	0	4	7
	Nonionic from example 6	0	3	0	0	0
	Nonionic from example 7	0	0	4	1	0
	Cocamide MEA	0	0.68	0.68	0.8	0
20	PEG 14M	0.1	0.35	0.5	0.1	0
	Cocoamidopropylbetaine	2.5	2.5	0	0	1.5
	Cetylalcohol	0.42	0.42	0.42	0.5	0.5
	Stearylalcohol	0.18	0.18	0.18	0.2	0.18
	Ethylene glycol distearate	1.5	1.5	1.5	1.5	1.5
25	Dimethicone ¹	1.75	1.75	1.75	1.75	2.0
	Perfume solution	0.45	0.45	0.45	0.45	0.45
	DMDM hydantoin	0.37	0.37	0.37	0.37	0.37
	Color solution (ppm)	64	64	64	64	64
	Water and minors	----- q. s. to 100% -----				

30

1. Dimethicone is a 40(gum)/60(fluid) weight ratio blend of SE-76 dimethicone gum available from General Electric Silicones Division and a dimethicone fluid having a viscosity of 350 centistokes.

5 EXAMPLES 17 to 32: Granular Laundry Detergents

The following laundry detergent compositions are prepared in accord with the invention:

	17	18	19	20	21	22
MBAS _{14.4}	8.0	4.0	4.0	8.0	4.0	4.0
C45AS	-	4.0	2.8	-	4.0	2.8
LAS	-	-	1.2	-	-	1.2
Nonionic from example 4	-	3.4	-	1.7	-	-
Nonionic from example 1	3.4	-	-	1.7	-	3.4
Nonionic from example 2(b)	-	-	3.4	-	3.4	-
AQA	0.4	0.5	0.6	0.8	0.8	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.5	1.5	1.5	1.5
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3

CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

The following laundry detergent compositions are prepared in accord with the invention:

	23	24	25	26	27
MBAS14.4	22	16.5	11	1 - 5.5	10 - 25
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES MBAE2S14.3	0	1 - 5.5	11	16.5	0 - 5
AQA	2	2	2	2	0.5 - 4
Nonionic from example 2g	-	1.5	-	-	1 - 4
Nonionic from example 5	1.5	-	-	1.5	1 - 4
Nonionic from example 1	-	-	1.5	-	1 - 4
Zeolite A	27.8	27.8	27.8	27.8	20 - 30
PAA	2.3	2.3	2.3	2.3	0 - 5

Carbonate	27.3	27.3	27.3	27.3	20 - 30
Silicate	0.6	0.6	0.6	0.6	0 - 2
PB1	1.0	1.0	1.0	1.0	0 - 3
Protease	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5
Cellulase	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.5
Amylase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 1
SRP 1	0.4	0.4	0.4	0.4	0 - 1
Brightener 1 or 2	0.2	0.2	0.2	0.2	0 - 0.3
PEG	1.6	1.6	1.6	1.6	0 - 2
Sulfate	5.5	5.5	5.5	5.5	0 - 6
Silicone Antifoam	0.42	0.42	0.42	0.42	0 - 0.5
Moisture & Minors	---Balance---				
Density (g/L)	663	663	663	663	600 - 700

The following laundry detergent compositions are prepared in accord with the invention:

	28	29	30	31	32
MBAS14.4	16.5	12.5	8.5	4	1 - 25
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES MBAE2S14.3	0 - 6	10	14	18.5	0 - 20
AQA	2	2	2	2	1 - 4
TFAA	1.6	1.6	1.6	1.6	0 - 4
Nonionic from example 6	5	-	-	5	1 - 6

Nonionic from example 4	-	5	-	-	1 - 6
Nonionic from example 3	-	-	5	-	1 - 6
Zeolite A	15	15	15	15	10 - 30
NaSKS-6	11	11	11	11	5 - 15
Citrate	3	3	3	3	0 - 8
MA/AA	4.8	4.8	4.8	4.8	0 - 8
HEDP	0.5	0.5	0.5	0.5	0 - 1
Carbonate	8.5	8.5	8.5	8.5	0 - 15
Percarbonate or PB1	20.7	20.7	20.7	20.7	0 - 25
TAED	4.8	4.8	4.8	4.8	0 - 8
Protease	0.9	0.9	0.9	0.9	0 - 1
Lipase	0.15	0.15	0.15	0.15	0 - 0.3
Cellulase	0.26	0.26	0.26	0.26	0 - 0.5
Amylase	0.36	0.36	0.36	0.36	0 - 0.5
SRP 1	0.2	0.2	0.2	0.2	0 - 0.5
Brightener 1 or 2	0.2	0.2	0.2	0.2	0 - 0.4
Sulfate	2.3	2.3	2.3	2.3	0 - 25
Silicone Antifoam		0.4	0.4	0.4	0 - 1
Moisture & Minors	---Balance---				
Density (g/L)	850	850		850	850

EXAMPLES 33 to 40: Hard Surface Cleaners

Mixing the listed ingredients in the listed proportions made the following compositions.

These compositions were used neat to clean marble and dilute to clean lacquered wooden

5 floors. Excellent cleaning and surface safety performance was observed.

	33	34	35	36	37	38	39	40
Nonionic from example 8	3.0	-	1.0	-	3.2	-	-	-
Nonionic from example 1	-	3.0	2.0	-	-	-	4.0	8.0

Nonionic from example 3	-	-	2.0	3.2	-	3.2	4.0	-
C23E3	1.0	1.0	1.5	1.3	1.3	1.5	3.0	3.5
C24E21	2.0	2.0	2.5	1.9	1.9	2.0	5.0	6.0
NaPS	2.0	1.5	1.2	1.2	1.0	1.7	3.0	2.5
NaTS	1.2	3.0	2.2	2.0	2.0	1.5	4.0	5.0
MgSO4	0.20	0.9	0.30	0.50	1.3	2.0	1.0	3.0
Citrate	0.3	1.0	0.5	0.75	1.8	3.0	1.5	6.0
NaHCO3	0.06	0.1	-	0.1	-	0.2	-	-
Na2HPO4	-	-	0.1	-	0.3	-	-	-
Na2H2P2O7	-	-	-	-	-	-	0.2	0.5
pH	8.0	7.5	7.0	7.25	8.0	7.4	7.5	7.2
Water and Minors	q.s. to 100%							

EXAMPLE 41

Automatic dishwashing compositions:

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>A</u>	<u>B</u>
Sodium Tripolyphosphate (STPP)	24.0	45.0
Sodium Carbonate	20.0	13.5
Hydrated 2.0r Silicate	15.0	13.5
Nonionic Surfactant ¹	3.0	3.0
C ₁₄ Amine Oxide	1.0	1.0
Polymer ²	4.0	--
Protease (4% active)	0.83	0.83
Amylase (0.8% active)	0.5	0.5
Perborate Monohydrate (15.5% active AvO) ³	14.5	14.5
Cobalt Catalyst ⁴	0.008	--

Dibenzoyl Peroxide (18% active)	4.4	4.4
Water, Sodium Sulfate, Misc.	Balance	Balance

¹ Nonionic surfactant according to Example 1.

² Terpolymer selected from either 60% acrylic acid/20% maleic acid/20% ethyl acrylate, or 70% acrylic acid/10% maleic acid/20% ethyl acrylate.

5 ³ The AvO level of the above formula is 2.2%.

⁴ Pentaamineacetatocobalt(III) nitrate prepared as described hereinbefore; may be replaced by MnTacN.

10 The following examples further illustrate phosphate built ADD compositions which contain a bleach/enzyme particle, but are not intended to be limiting thereof. These compositions are suitable for use in the methods of the present invention. All percentages noted are by weight of the finished compositions, other than the perborate (monohydrate) component, which is listed as AvO.

EXAMPLES 42-43

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>42</u>	<u>43</u>
STPP	30.0	32.0
Na ₂ CO ₃	30.5	20.5
2 R Silicate (SiO ₂)	8.0	4.0
Catalyst ¹	0.008	0.004
Savinase TM 12T	--	1.1
Protease D	0.9	--
Perborate (AvO)	5.0	0.7
Polymer ²	4.0	--
Dibenzoyl Peroxide	0.2	0.15
Paraffin	0.5	0.5

Benzotriazole	0.10	0.3
C ₁₄ Amine Oxide	0.5	0.5
Nonionic Surfactant ³	2.0	2.0
Sodium Sulfate, Moisture	-----	Balance -----

¹ Pentaamineacetatocobalt(III) nitrate; may be replaced by MnTacN.

² Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers.

³ Nonionic surfactant according to Example 7.

In compositions of Examples 42 and 43, respectively, the catalyst and enzymes are introduced into the compositions as 200-2400 micron composite particles that are prepared by spray coating, fluidized bed granulation, marumarizing, prilling, or flaking/grinding operations. If desired, the protease and amylase enzymes may be separately formed into their respective catalyst/enzyme composite particles, for reasons of stability, and these separate compositions added to the compositions.

The following examples further illustrate ADD granular compositions with chlorine bleach suitable for use in the methods of this present invention.

EXAMPLE 44-45

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>44</u>	<u>45</u>
STPP	25	31
Na ₂ CO ₃	23.0	15.0
2 R Silicate (SiO ₂)	17.5	25.0
Hypochlorite	1.0	3.0
Polymer ¹	2.0	--
Dibenzoyl Peroxide	--	0.15
Paraffin	1.0	1.0
C ₁₆ Amine Oxide	0.5	1.0
Nonionic Surfactant ²	2.0	3.0

Sodium Sulfate, Moisture

----- Balance -----

¹ Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers³ Nonionic surfactant according to Example 8.

The following examples further illustrate ADD liquid-gel compositions suitable for use in the methods of this present invention.

5

EXAMPLES 46-47Ingredients:Weight %

	<u>46</u>	<u>47</u>
STPP	32.0	25.0
Na ₂ CO ₃	0.7	2.0
2 R Silicate (SiO ₂)	0.3	1.0
Savinase™ 12T	2.0	1.0
Termamyl™	1.4	0.5
Perborate (AvO)	3.5	--
C ₁₄ Amine Oxide	0.8	0.8
Nonionic Surfactant ¹	3.5	3.5
Sodium Sulfate, Moisture	----- Balance -----	

¹ Nonionic surfactant according to Example 3.

The following examples further illustrate ADD rinse aid compositions suitable for use in the methods of this present invention.

10

EXAMPLES 48-49Ingredients:Weight %

	<u>48</u>	<u>49</u>
Citric Acid	10.0	15.0
Ethanol	5.0	10.0
HEDP Acid ¹	1.0	0.7
Sodium Cumene Sulfonate	15.0	10.0

Polymer ²	--	1.0
C ₁₄ Amine Oxide	2.0	0.5
Nonionic Surfactant ³	8.0	8.0
Nonionic Surfactant ⁴	6.0	-
Moisture	-----	Balance -----

¹ 1-Hydroxyethylidene-1,1-diphosphonic acid

² Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers

³ Nonionic surfactant according to Example 1.

⁴ Nonionic surfactant according to Example 5.

- 5 The following examples further illustrate ADD tablet compositions suitable for use in the methods of this present invention.

EXAMPLES 54-55

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>50</u>	<u>51</u>
STPP	48.0	30
Na ₂ CO ₃	15.0	25.0
2 R Silicate (SiO ₂)	4.0	8.0
Catalyst ¹	0.008	0.004
Savinase TM 12T	--	1.0
Termamyl TM	0.6	0.5
Perborate (AvO)	10.0	15.0
Polymer ²	2.0	2.0
Dibenzoyl Peroxide	0.2	0.15
Paraffin	1.0	1.0
Benzotriazole	0.5	0.5
C ₁₄ Amine Oxide	1.0	1.0

Sodium Sulfate, Moisture ----- Balance -----

² Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers

³ Nonionic surfactant according to Example 2f.

[illegible]